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Kaye et al.

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(54) **HIGH ENERGY MATERIALS FOR A BATTERY AND METHODS FOR MAKING AND USE**

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- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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- (60) Provisional application No. 61/786,602, filed on Mar. 15, 2013.

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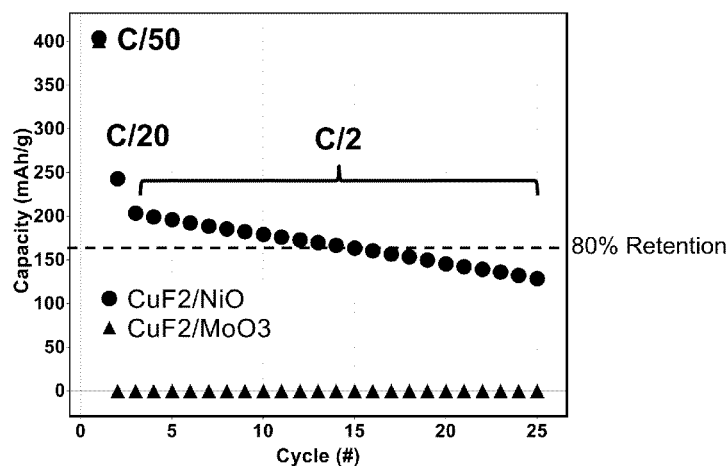
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CPC **H01M 4/366** (2013.01); **C04B 35/553**
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- (58) **Field of Classification Search**
None
See application file for complete search history.

(57) **ABSTRACT**

A method of forming an electrode active material by reacting a metal fluoride and a reactant. The reactant can be a metal oxide, metal phosphate, metal fluoride, or a precursors expected to decompose to oxides. The method includes a milling step and an annealing step. The method can alternatively include a solution coating step. Also included is the composition formed following the method.

12 Claims, 19 Drawing Sheets



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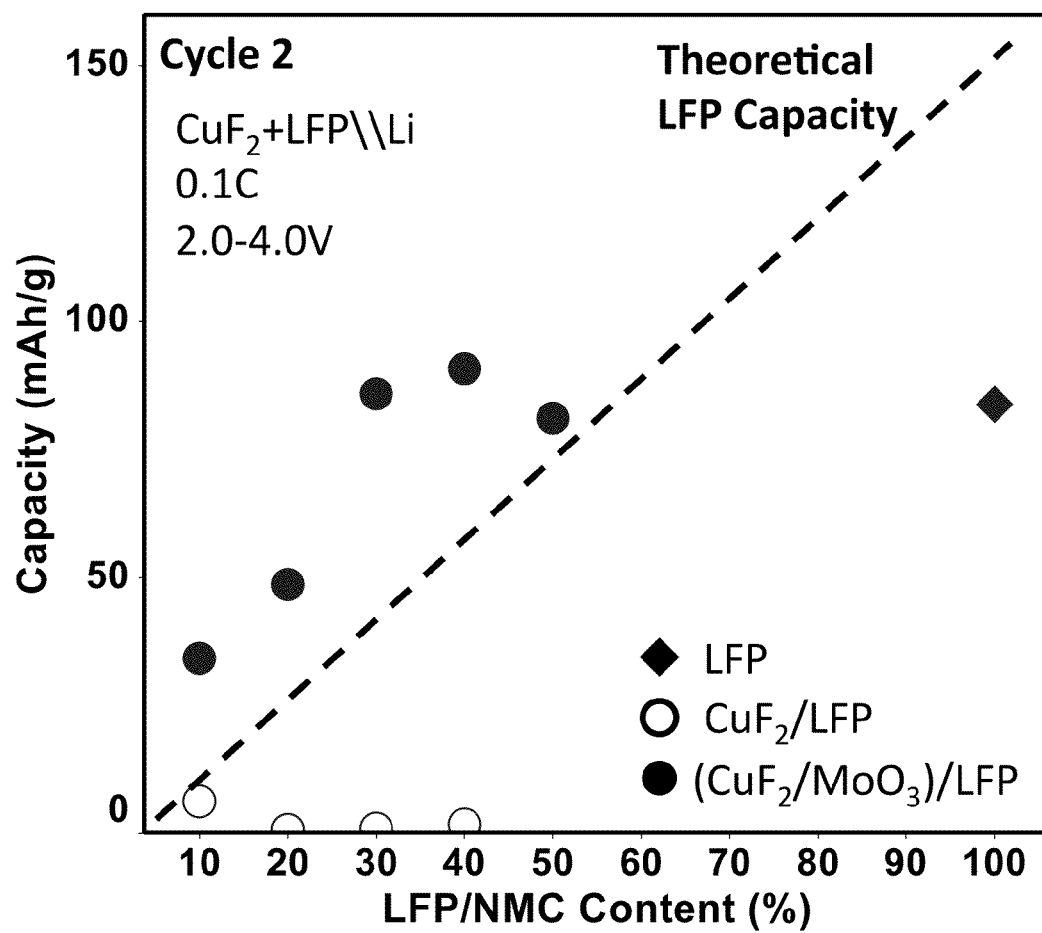


FIG. 1

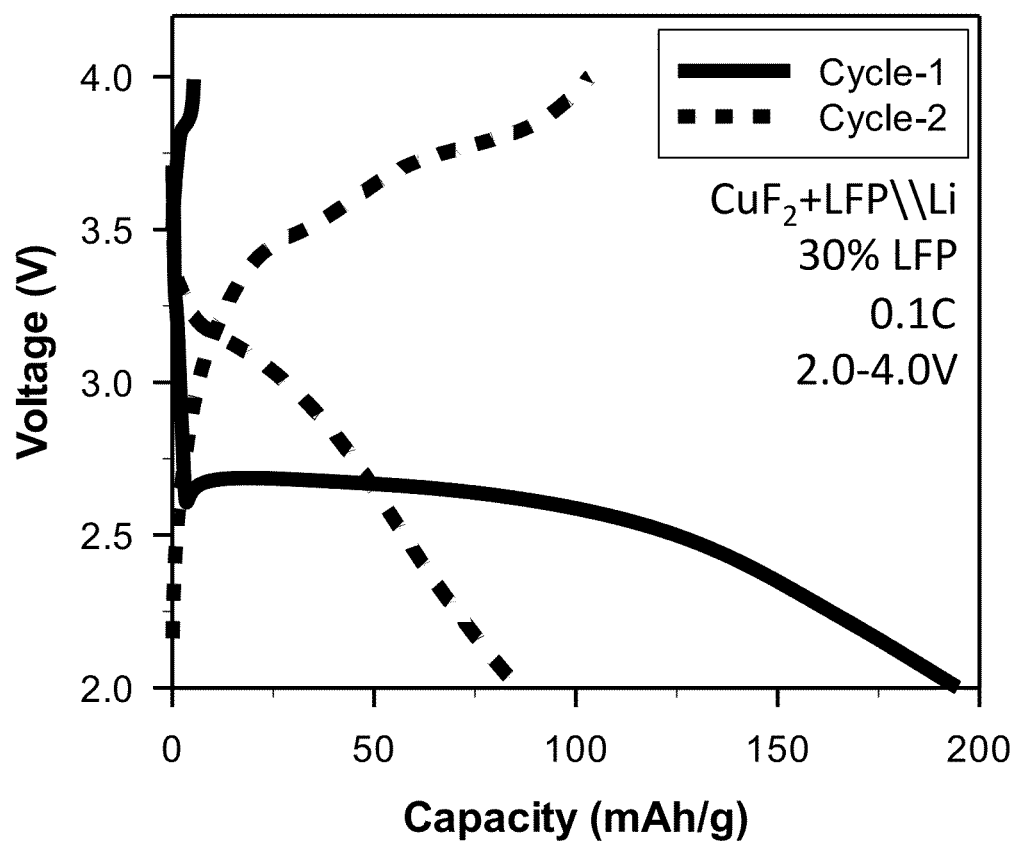


FIG. 2

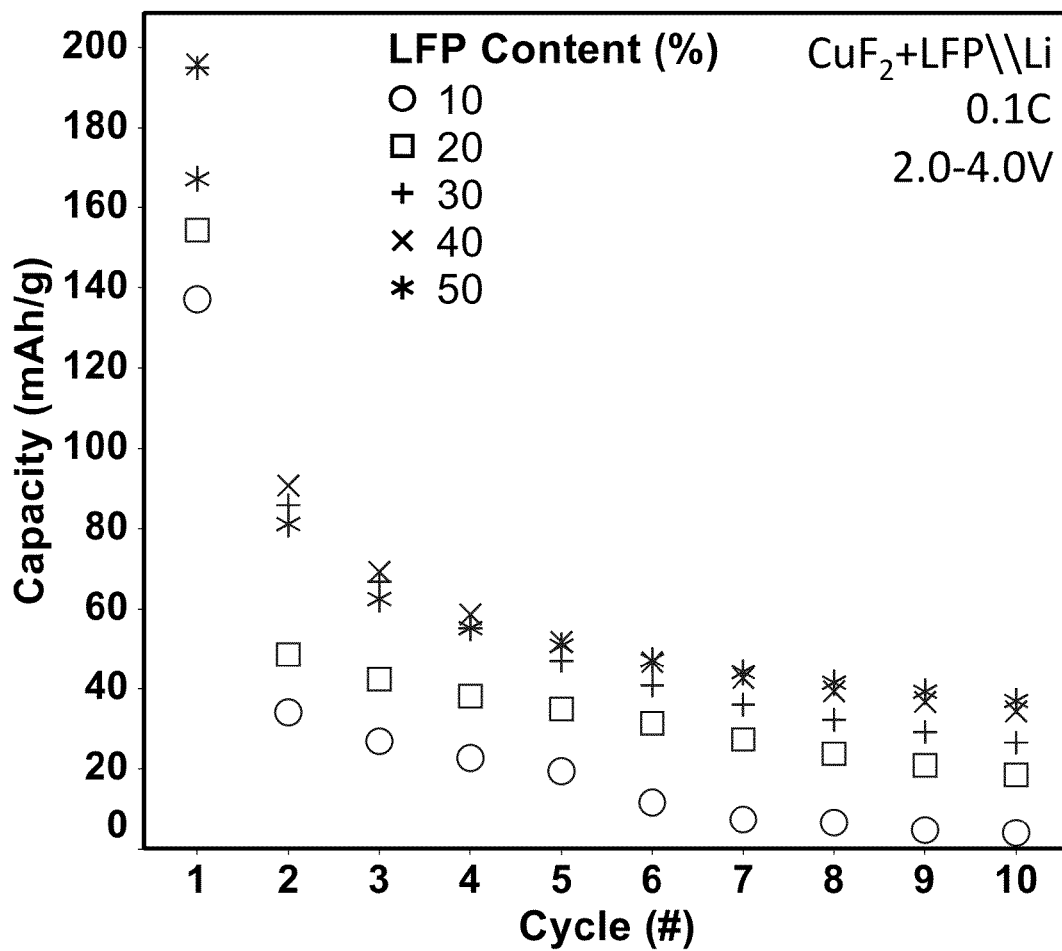


FIG. 3

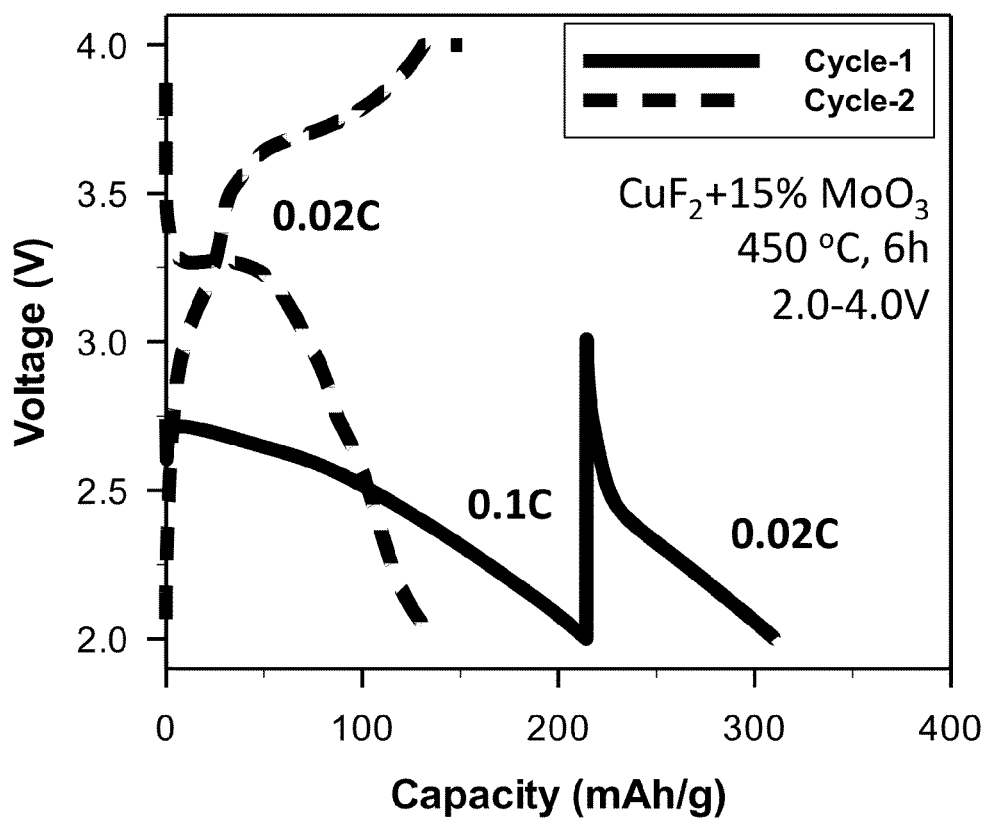
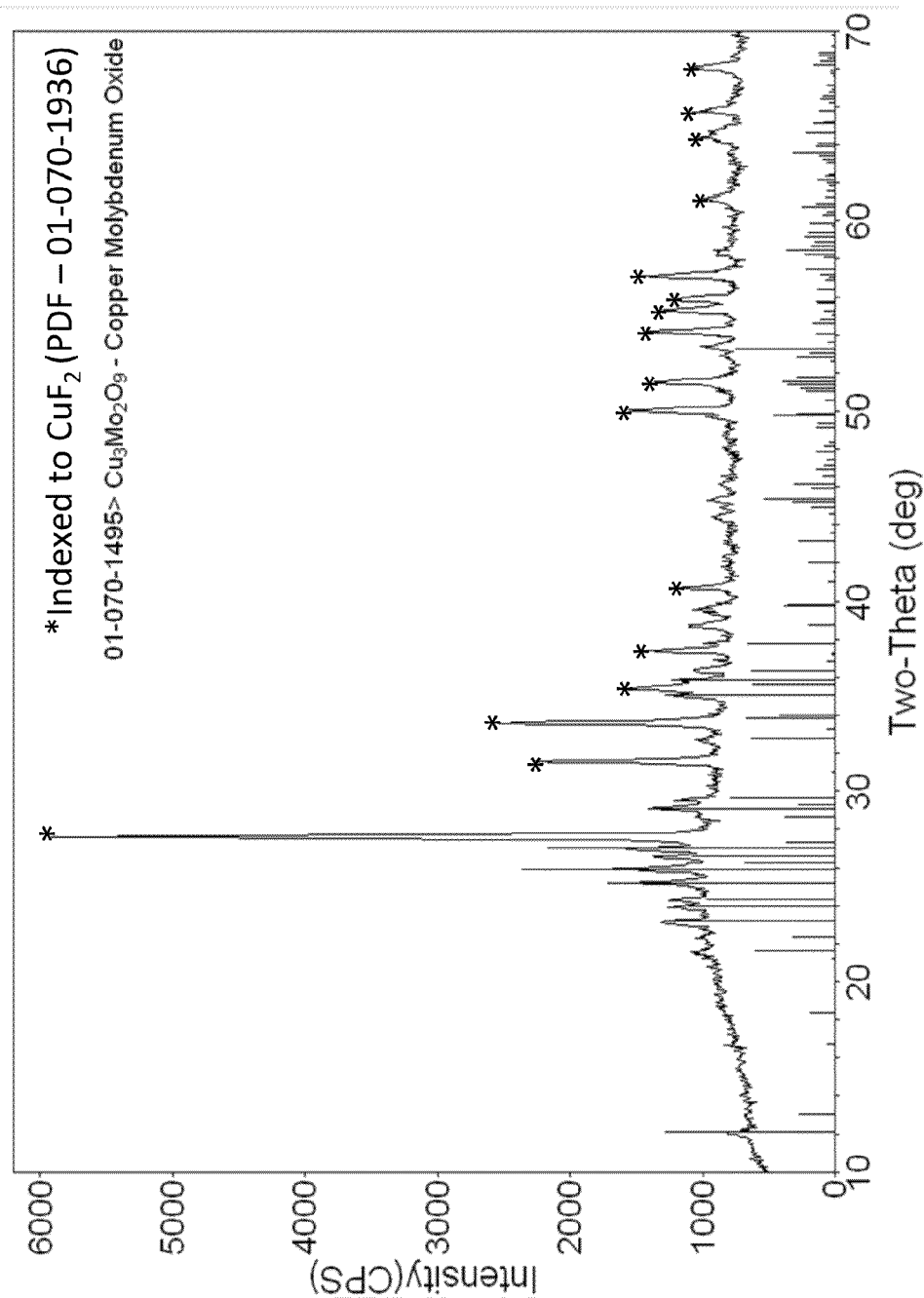


FIG. 4

FIG. 5



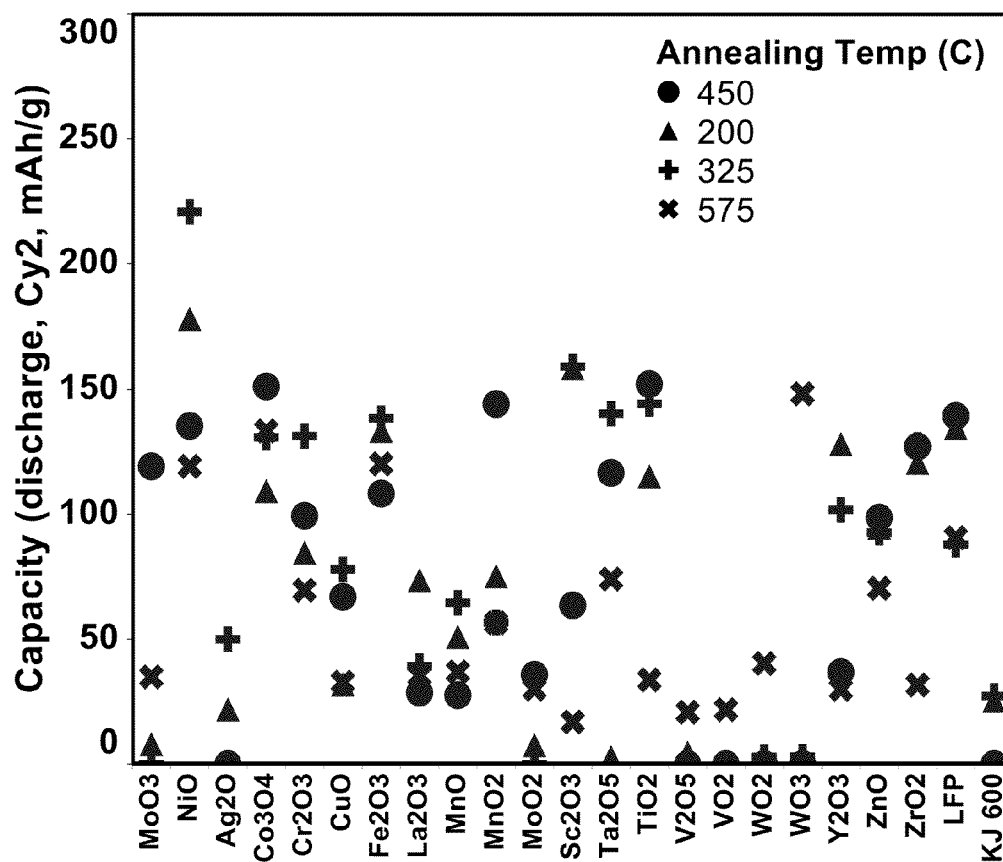


FIG. 6

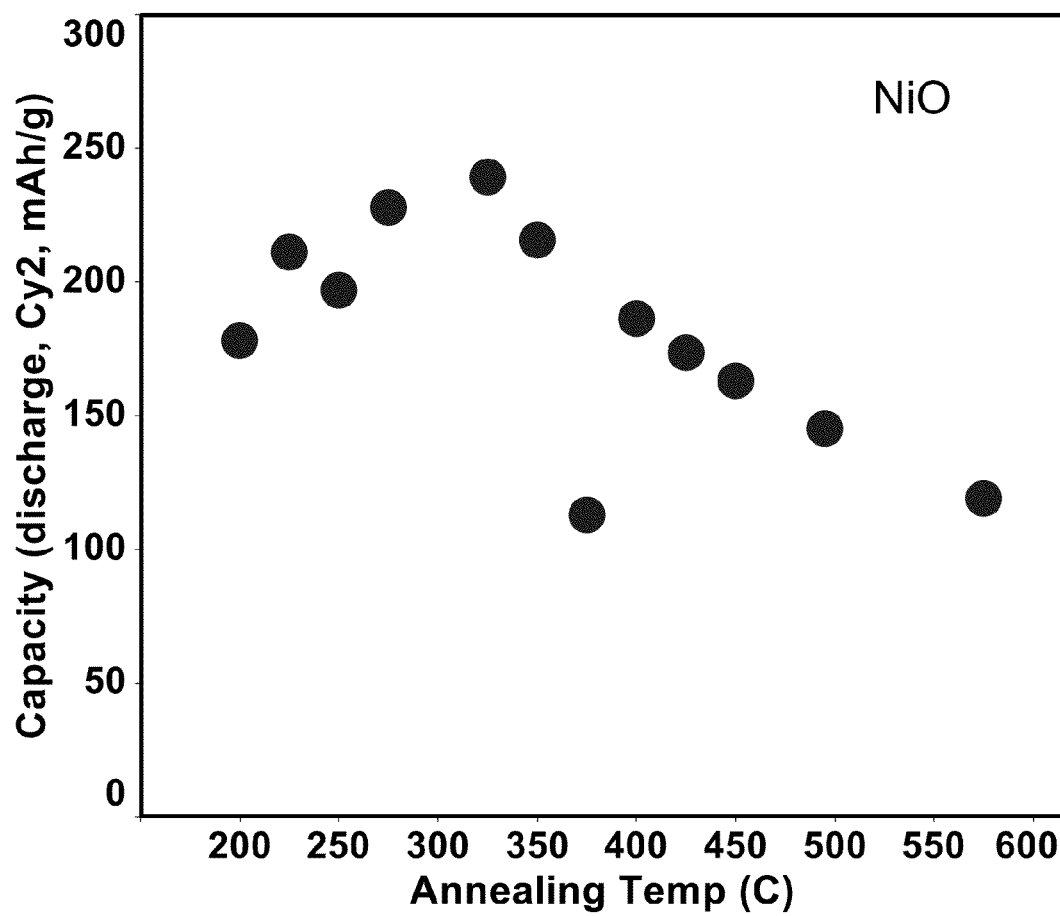
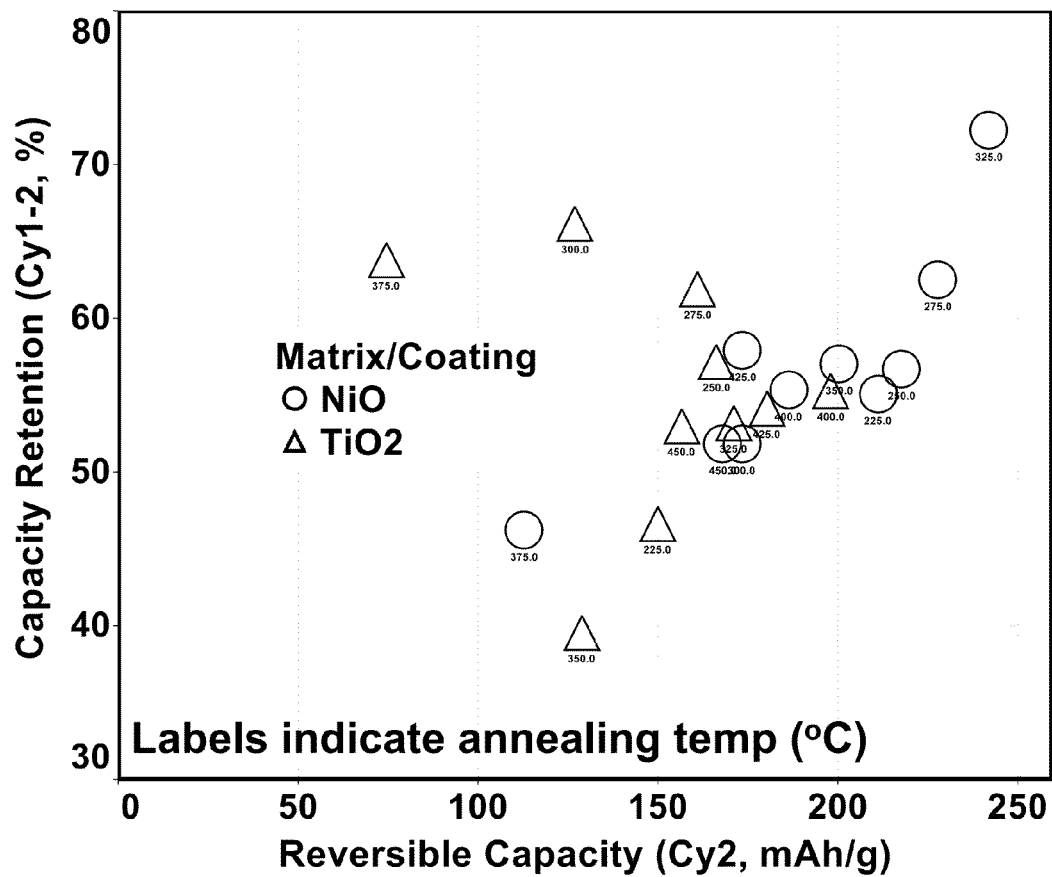


FIG. 7



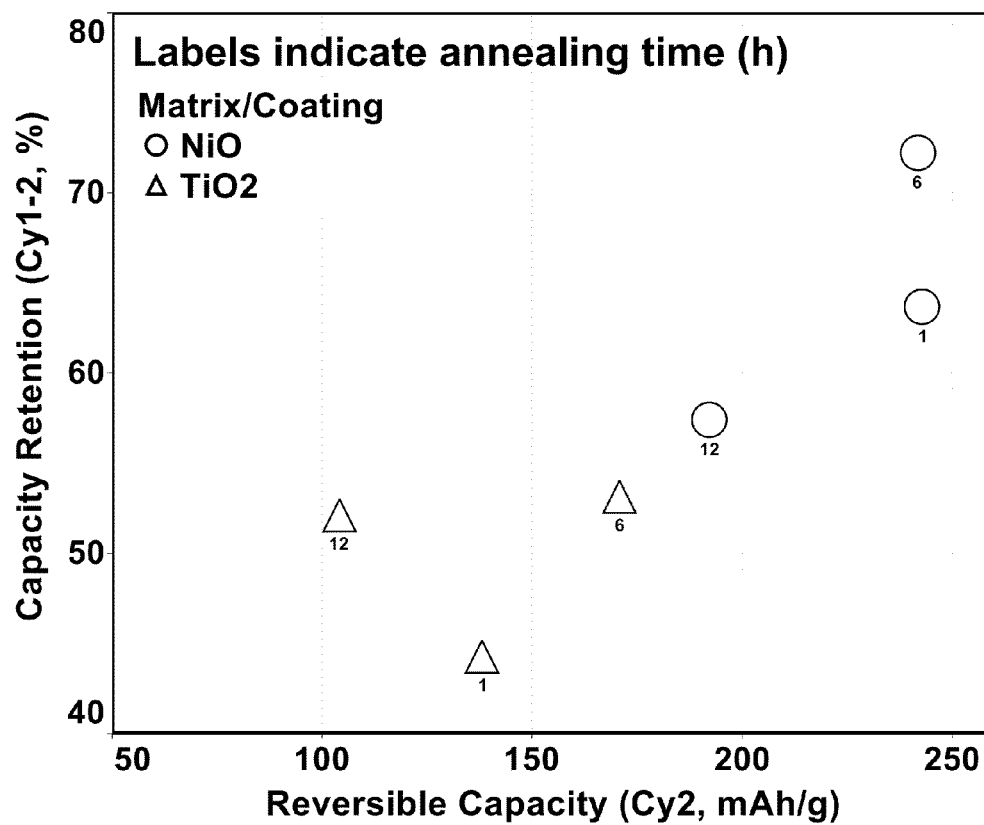


FIG. 9

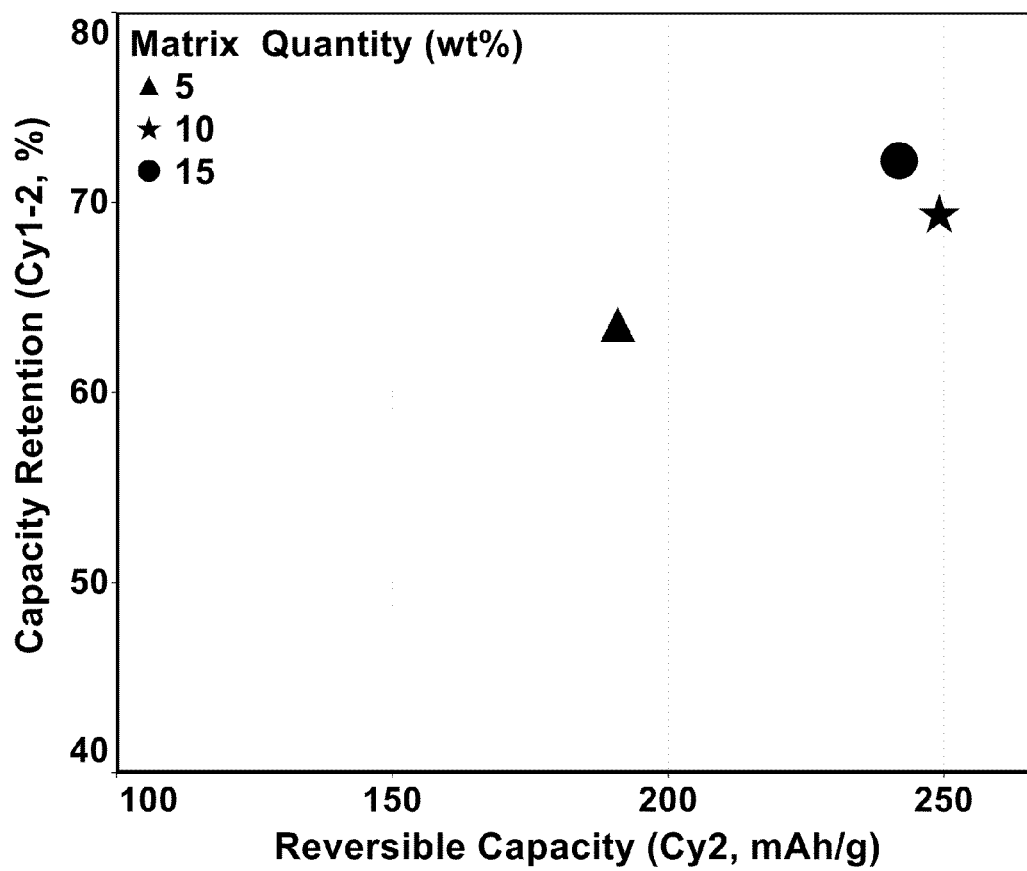


FIG. 10

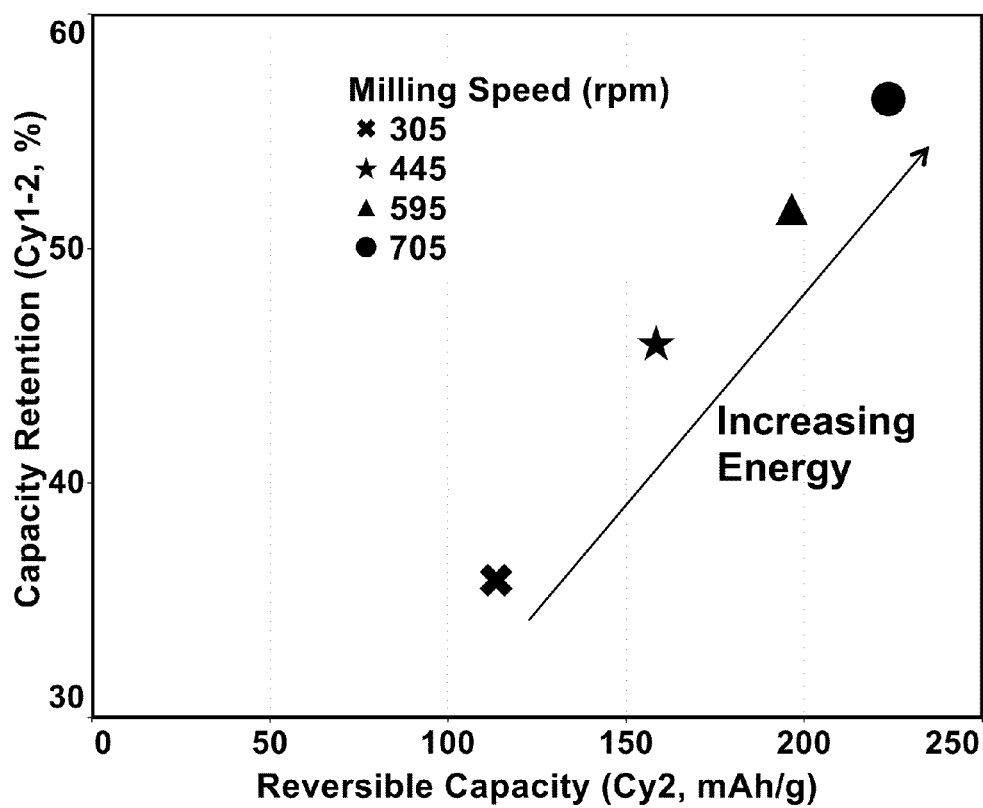


FIG. 11

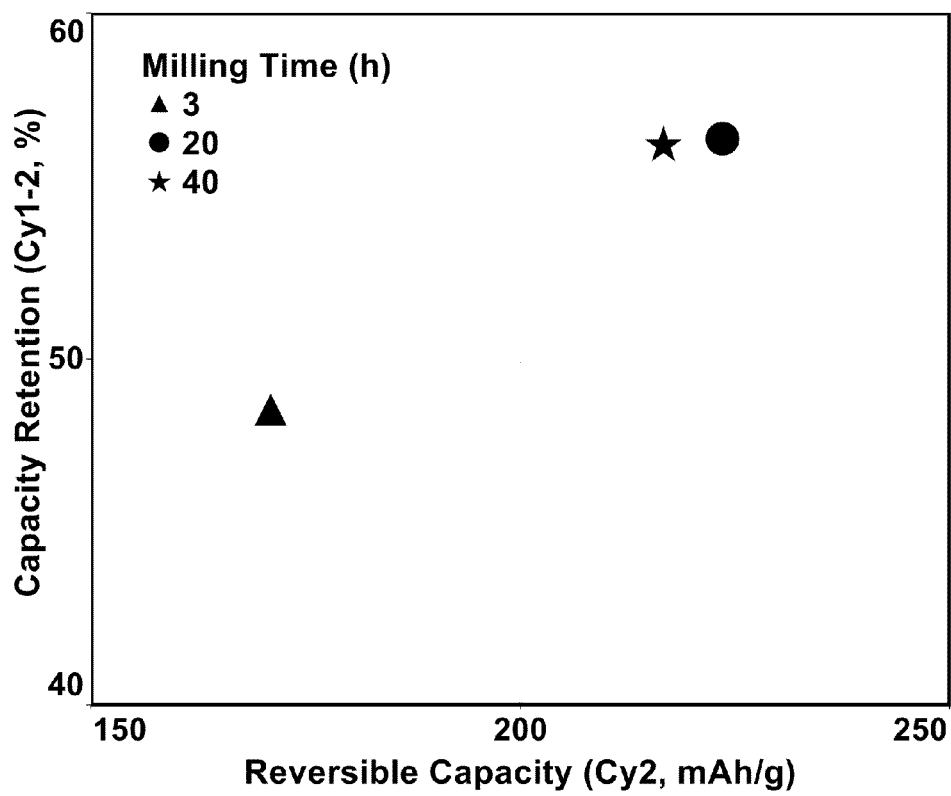


FIG. 12

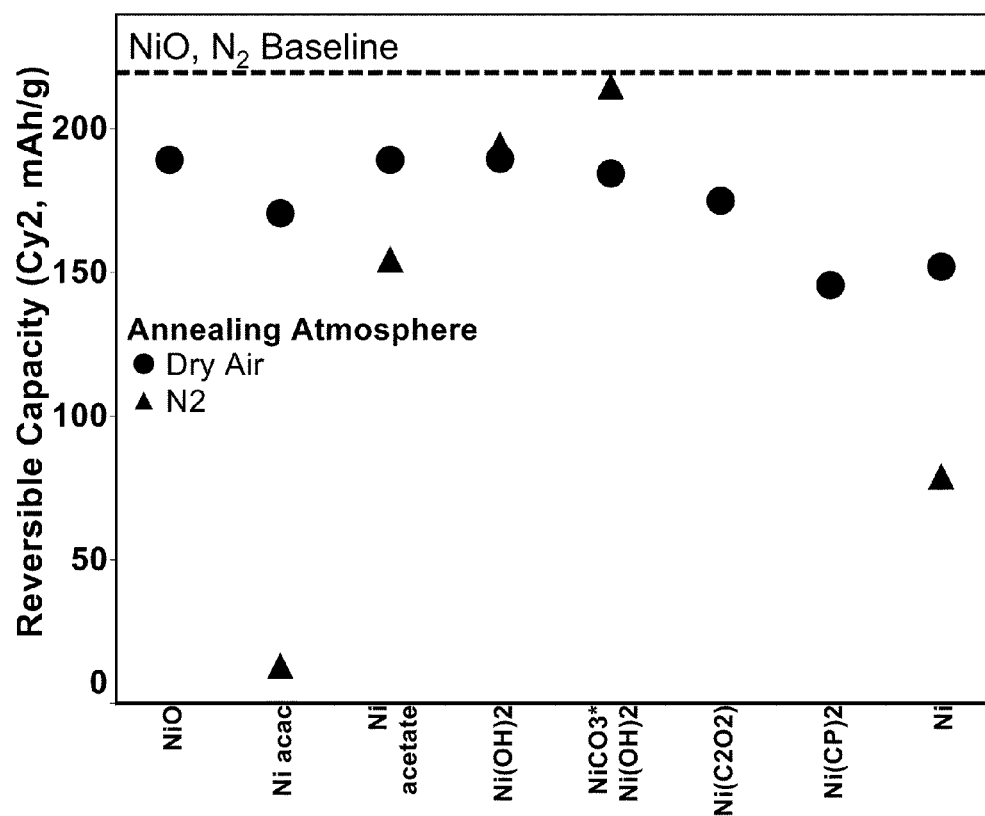


FIG. 13

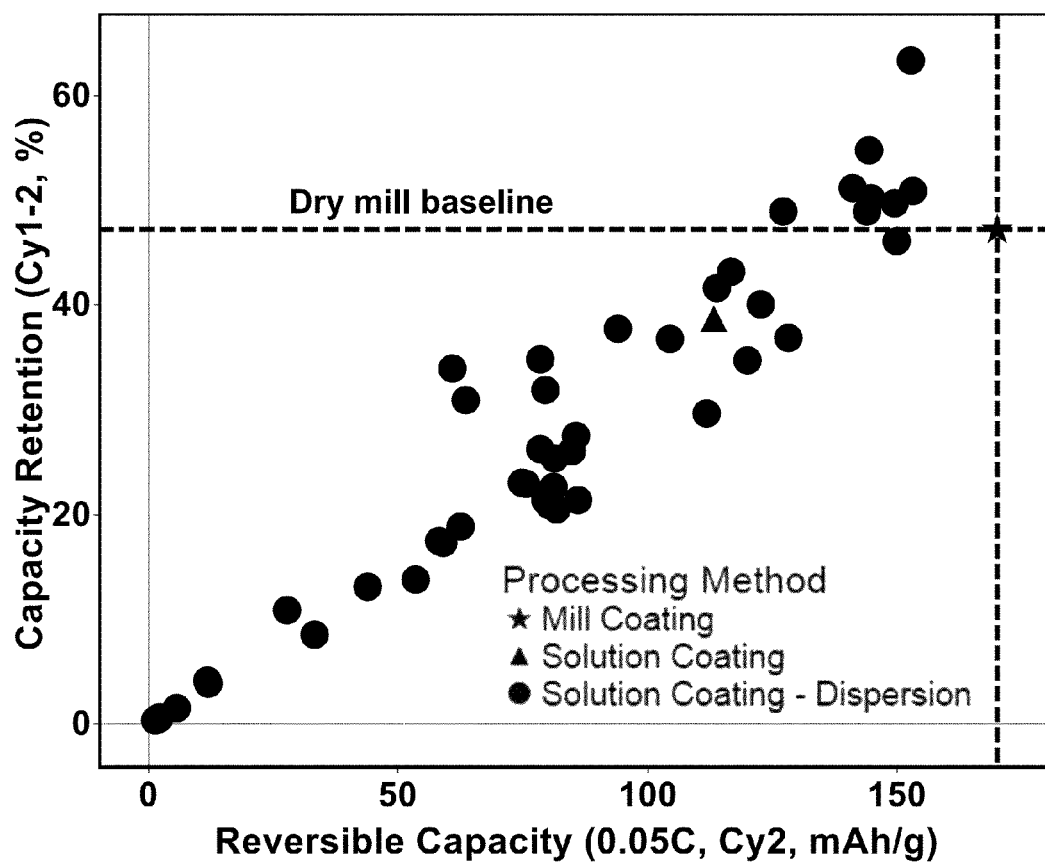


FIG. 14

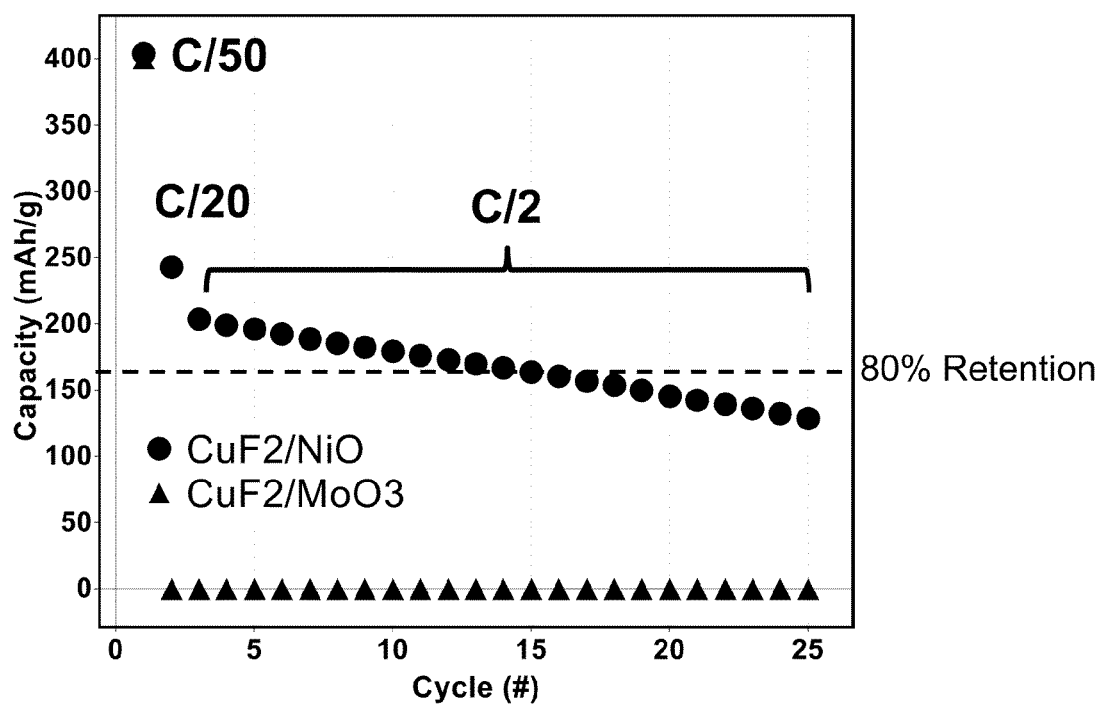


FIG. 15

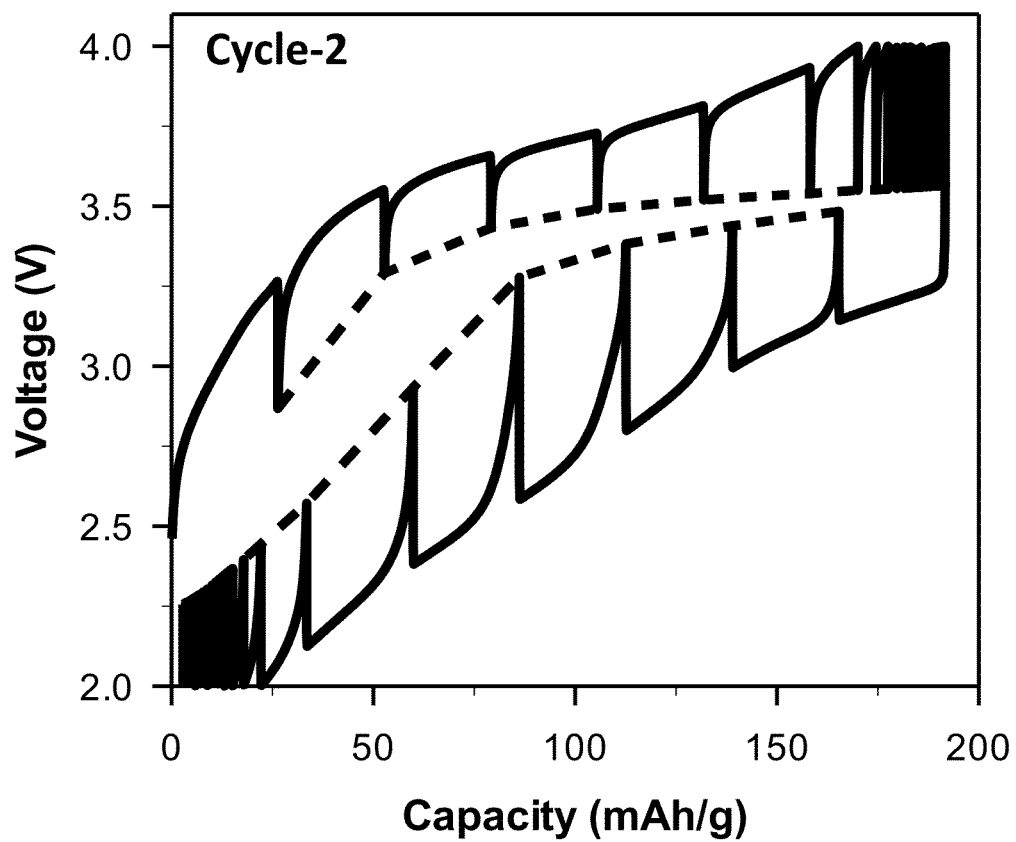


FIG. 16

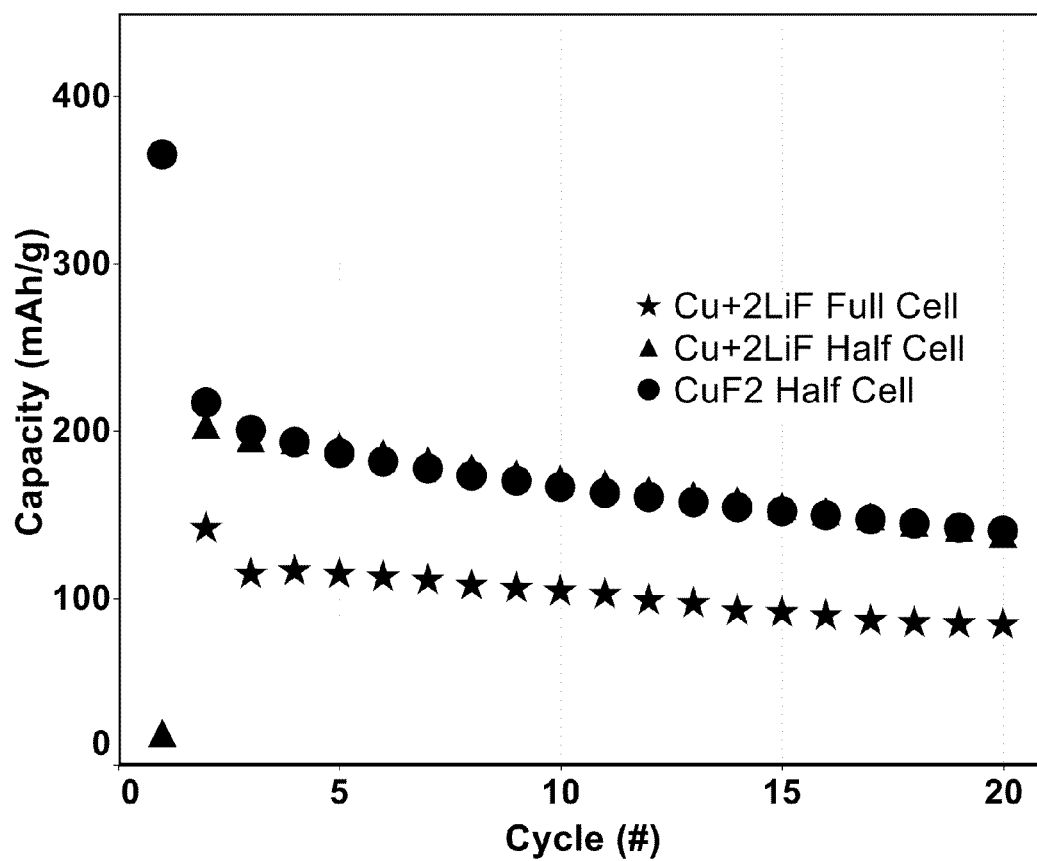


FIG. 17

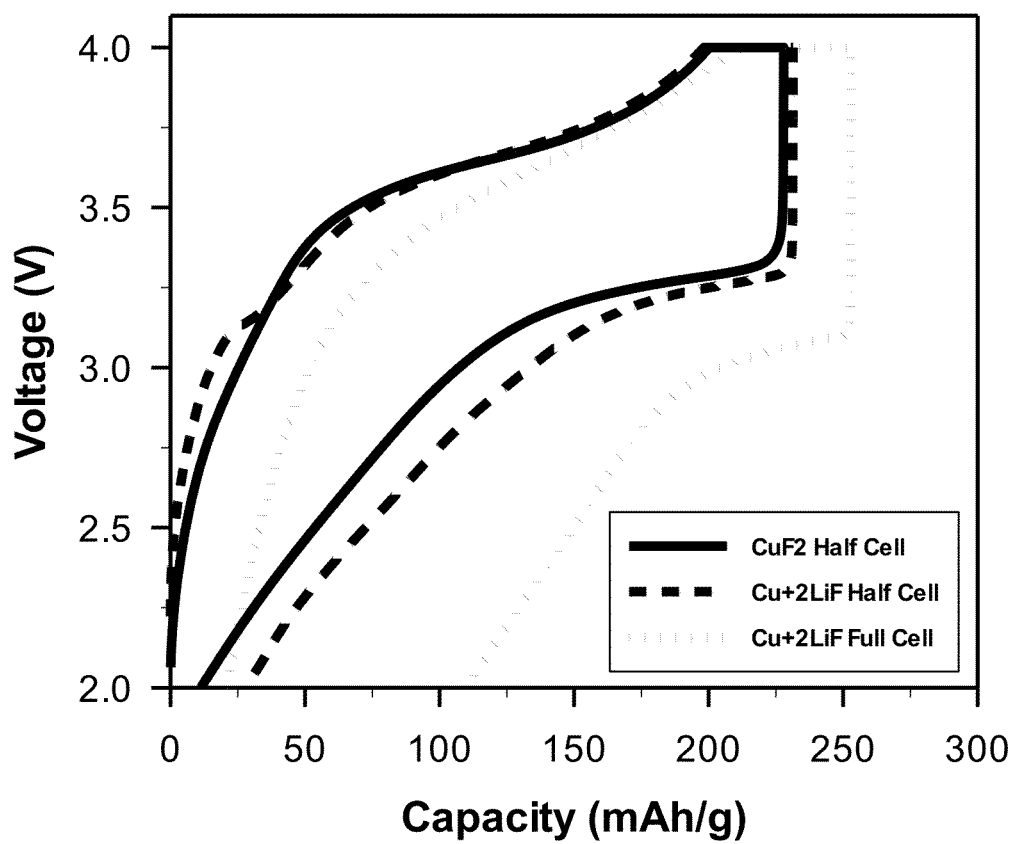


FIG. 18

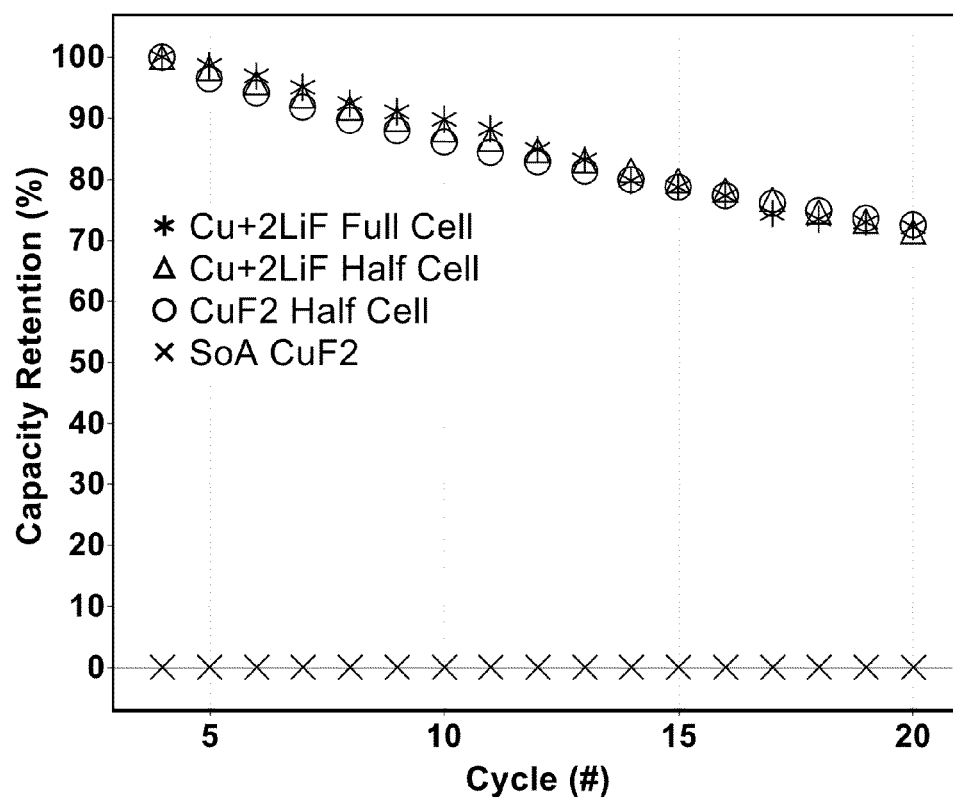


FIG. 19

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HIGH ENERGY MATERIALS FOR A BATTERY AND METHODS FOR MAKING AND USE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of International Application No. PCT/US2014/028506, having an international filing date of Mar. 14, 2014 entitled "High Energy Materials For A Battery And Methods For Making And Use," which claims priority to U.S. Provisional Application No. 61/786,602 filed Mar. 15, 2013 entitled "High Energy Materials For A Battery And Methods For Making And Use." This application claims priority to and the benefit of each of these applications, and each application is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

The present invention is in the field of battery technology, and more particularly in the area of materials for making high-energy electrodes for batteries, including metal-fluoride materials.

One type of battery consists of a negative electrode made primarily from lithium and a positive electrode made primarily from a compound containing a metal and fluorine. During discharge, lithium ions and electrons are generated from oxidation of the negative electrode while fluoride ions are produced from reduction of the positive electrode. The generated fluoride ions react with lithium ions near the positive electrode to produce a compound containing lithium and fluorine, which may deposit at the positive electrode surface.

Metal fluoride based batteries are an attractive energy storage technology because of their extremely high theoretical energy densities. For example, certain metal fluoride active materials can have theoretical energy densities greater than about 1600 Wh/kg or greater than about 7500 Wh/L. Further, metal fluorides have a relatively low raw material cost, for example less than about \$10/kg. However, a number of technical challenges currently limit their widespread use and realization of their performance potential.

One challenge for certain metal fluoride materials is comparatively poor rate performance. Many metal fluoride active materials have electrochemical potentials greater than about 2.5 V because of their relatively large bandgap produced by the highly ionic bonding between the metal and fluorine, and in particular between a transition metal and fluorine. Unfortunately, one of the drawbacks to wide bandgap materials is the intrinsically low electronic conductivity that results from the wide bandgap. As a result of this low conductivity, discharge rates of less than 0.1 C are required in order to obtain full theoretical capacity. More typically, discharge rates of 0.05 C to 0.02 C are reported in the literature. Such low discharge rates limit the widespread use of metal fluoride active materials.

Another challenge for certain metal fluoride active materials is a significant hysteresis observed between the charge and discharge voltages during cycling. This hysteresis is typically on the order of about 1.0V to about 1.5V. While the origin of this hysteresis is uncertain, current evidence suggests that kinetic limitations imposed by low conductivity play an important role. Further, asymmetry in the reaction paths upon charge and discharge may also play a role. Since the electrochemical potential for many of the metal fluorides

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is on the order of 3.0V, this hysteresis of about 1.0V to about 1.5V limits the overall energy efficiency to approximately 50%.

Limited cycle life is another challenge for certain metal fluoride active materials. Although rechargeability has been demonstrated for many metal fluoride active materials, their cycle life is typically limited to tens of cycles and is also subject to rapid capacity fade. Three mechanisms are currently believed to limit the cycle life for the metal fluoride active materials: agglomeration of metallic nanoparticles and mechanical stress due to volume expansion. It is believed that metal fluoride active materials can cycle by virtue of the formation during lithiation of a continuous metallic network within a matrix of insulating LiF. As the number of cycles increases, the metal particles tend to accumulate together into larger, discrete particles. The larger agglomerated particles in turn create islands that are electrically disconnected from one another, thus reducing the capacity and ability to cycle the metal fluoride active materials. The second limitation to extended cycle life is the mechanical stress imparted to the binder materials by the metal fluoride particles as a result of the volume expansion that occurs during the conversion reaction. Over time, the binder is pulverized, compromising the integrity of the cathode. Notably, for the metal fluoride CuF_2 , no demonstrations of rechargeability have been reported.

For CuF_2 , an additional challenge prevents rechargeability. The potential required to recharge a CuF_2 electrode is 3.55V. However, in typical electrolytes for lithium ion batteries, Cu metal oxidizes to Cu^{2+} at approximately 3.4 V vs. Li/Li^+ . The oxidized copper can migrate to the anode, where it is irreversibly reduced back to Cu metal. As a result, Cu dissolution competes with the recharge of $\text{Cu}+2\text{LiF}$ to CuF_2 , preventing cycling of the cell. The Cu metal accumulating on the anode surface can increase the impedance and/or destroy the solid-electrolyte interphase (SEI) on the anode.

The following papers and patents are among the published literature on metal fluorides that employ mixed conductors that are not electrochemically active within the voltage window of the metal fluoride: Badway, F. et al., *Chem. Mater.*, 2007, 19, 4129; Badway, F. et al., *J. Electrochem. Soc.*, 2007, 150, A1318; "Bismuth fluoride based nanocomposites as electrode materials" U.S. Pat. No. 7,947,392; "Metal Fluoride And Phosphate Nanocomposites As Electrode Materials" US 2008/0199772; "Copper fluoride based nanocomposites as electrode materials" US 2006/0019163; and "Bismuth oxyfluoride based nanocomposites as electrode materials" U.S. Pat. No. 8,039,149.

Certain embodiments of the present invention can be used to form electrochemical cells having metal fluoride active material that exhibit improved rate performance, improved energy efficiency, and improved cycle life when compared to prior batteries. Thus, these and other challenges can be addressed by embodiments of the present invention described below.

BRIEF SUMMARY OF THE INVENTION

Certain embodiments of the invention include a method of making a composition for use in forming a cathode for a battery. The method includes milling a metal fluoride material with a metal complex and annealing the mixture, wherein at least a portion of the metal fluoride material and at least a portion of the metal complex undergo a phase change. The method can include forming a coating on at least a portion of the metal fluoride material. The metal fluoride material is preferably CuF_2 . The metal complex can be a metal oxide selected from the group consisting of Al_2O_3 , SiO_2 , MoO_3 ,

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MoO₂, NiO, CuO, VO₂, V₂O₅, TiO₂. Preferably, the metal oxide is NiO. The annealing temperature is less than 450 degrees C., less than 400 degrees C., less than 325 degrees C., or less than 200 degrees C. Preferably, the annealing temperature is about 325 degrees C. The temperature is chosen such that it is sufficiently high for the metal complex to react with the metal fluoride, but not high enough to decompose the metal fluoride. Without such heat treatment and the resulting reaction, the material is not rechargeable, as is demonstrated by experiments described herein.

Certain embodiments of the invention include a composition formed by the methods disclosed herein. The composition is characterized by having reversible capacity. The composition can include particles with a grain size greater than 100 nm, 110 nm, 120 nm, or 130 nm. The composition can include a particle having a first phase and a coating on the particle having a second phase. Preferably, the first phase includes the metal fluoride and the second phase includes the metal oxide. The coating can be covalently bonded to the particle.

Certain embodiments of the invention include batteries having electrodes formed from the compositions disclosed herein, the method of making such batteries, and the method of use of such batteries.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

FIG. 1 illustrates electrochemical characterization of different hybrid cathode formulations according to embodiments of the invention in which the content of a conductive matrix material is varied in the cathode.

FIG. 2 illustrates electrochemical characterization of a cathode formulation from FIG. 1 in which the voltage of a hybrid cathode according to embodiments of the invention is plotted against the capacity for the first and second cycles.

FIG. 3 illustrates electrochemical characterization of different hybrid cathode formulations according to embodiments of the invention in which the discharge is plotted as a function of cycle for 10 cycles.

FIG. 4 illustrates electrochemical characterization of a hybrid cathode formed from a metal fluoride and a reactant material according to certain embodiments. The cathode demonstrates rechargeability.

FIG. 5 illustrates a powder X-ray diffraction pattern of a material used to form a rechargeable metal fluoride cathode.

FIG. 6 illustrates second cycle discharge capacity for a variety of hybrid cathode materials used according to embodiments of the invention.

FIG. 7 illustrates second cycle discharge capacity for a hybrid cathode material used according to embodiments of the invention versus annealing temperature.

FIG. 8 illustrates second cycle the capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt % CuF₂ with 15 wt % of certain metal oxides (in this case NiO or TiO₂) at certain annealing temperatures.

FIG. 9 illustrates the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt % CuF₂ with 15 wt % of certain metal oxides (in this case NiO or TiO₂) for certain annealing times.

FIG. 10 illustrates the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, 90 wt %, or 95 wt % CuF₂ with 5 wt %, 10 wt %, 15 wt % of NiO.

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FIG. 11 illustrates the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO as a function of milling energy.

FIG. 12 illustrates the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO as a function of milling time.

FIG. 13 illustrates the second cycle reversible capacity measured for various starting materials used to react with CuF₂.

FIG. 14 illustrates the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting CuF₂ with nickel(II) acetylacetonate using various processing conditions.

FIG. 15 illustrates the capacity as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO and for a control material.

FIG. 16 illustrates a galvanostatic intermittent titration technique measurement for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO.

FIG. 17 illustrates the capacity of full cells and half cells as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO.

FIG. 18 illustrates voltage traces of the full cell and half cells prepared as described in relation to FIG. 17.

FIG. 19 illustrates the capacity retention of full cells and half cells as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO.

DETAILED DESCRIPTION OF THE INVENTION

The following definitions apply to some of the aspects described with respect to some embodiments of the invention. These definitions may likewise be expanded upon herein. Each term is further explained and exemplified throughout the description, figures, and examples. Any interpretation of the terms in this description should take into account the full description, figures, and examples presented herein.

The singular terms "a," "an," and "the" include the plural unless the context clearly dictates otherwise. Thus, for example, reference to an object can include multiple objects unless the context clearly dictates otherwise.

The terms "substantially" and "substantial" refer to a considerable degree or extent. When used in conjunction with an event or circumstance, the terms can refer to instances in which the event or circumstance occurs precisely as well as instances in which the event or circumstance occurs to a close approximation, such as accounting for typical tolerance levels or variability of the embodiments described herein.

The term "about" refers to the range of values approximately near the given value in order to account for typical tolerance levels, measurement precision, or other variability of the embodiments described herein.

The terms "conductive," "conductor," "conductivity," and the like refer to the intrinsic ability of a material to facilitate electron or ion transport and the process of doing the same. The terms include materials whose ability to conduct electricity may be less than typically suitable for conventional electronics applications but still greater than an electrically-insulating material.

The term "active material" and the like refers to the material in an electrode, particularly in a cathode, that donates, liberates, or otherwise supplies the conductive species during an electrochemical reaction in an electrochemical cell.

The term "transition metal" refers to a chemical element in groups 3 through 12 of the periodic table, including scandium

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(Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), cadmium (Cd), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), mercury (Hg), rutherfordium (Rf), dubnium (Db), seaborgium (Sg), bohrium (Bh), hassium (Hs), and meitnerium (Mt).

The term "halogen" refers to any of the chemical elements in group 17 of the periodic table, including fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At).

The term "chalcogen" refers to any of chemical elements in group 16 of the periodic table, including oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and polonium (Po).

The term "alkali metal" refers to any of the chemical elements in group 1 of the periodic table, including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr).

The term "alkaline earth metals" refers to any of the chemical elements in group 2 of the periodic table, including beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

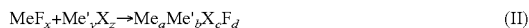
The term "rare earth element" refers to scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

A rate "C" refers to either (depending on context) the discharge current as a fraction or multiple relative to a "1 C" current value under which a battery (in a substantially fully charged state) would substantially fully discharge in one hour, or the charge current as a fraction or multiple relative to a "1 C" current value under which the battery (in a substantially fully discharged state) would substantially fully charge in one hour.

In certain embodiments, a novel active material, which may be referred to as a matrix material or a coated material or a hybrid material, is prepared for use in a cathode with metal fluoride (MeF_x) active materials. In some embodiments, the novel active material is prepared by combining a metal fluoride and a metal complex, followed by heat treatment of the mixture under an inert atmosphere according to the Formula (I)



According to certain embodiments, the heat treatment of the metal fluoride and metal complex causes a reaction to form a new phase according to the formula (II)



where x, y, z, a, b, and c depend on the identity and valence of the Me, Me', and X. In some instances, $0 < a \leq 1$, $0 < b \leq 1$, $0 \leq c \leq 1$, and $0 \leq d \leq 1$. In other embodiments, the heat treatment causes the formation of covalent bonds between the metal fluoride and the metal complex, improving conductivity and passivating the surface.

Suitable metal complexes, which can act as precursors for the reaction described herein, for use in synthesizing the matrix, coating, or active material include, but are not limited to, MoO_3 , MoO_2 , NiO , CuO , VO_2 , V_2O_5 , TiO_2 , Al_2O_3 , SiO_2 , LiFePO_4 , LiMe_7PO_4 (where Me_7 is one or more transition metal(s)), metal phosphates, and combinations thereof. According to embodiments of the invention, these oxides can be used in Formula (I).

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It is understood that the synthetic route for achieving the matrix, coating, hybrid, or active matrix material may vary, and other such synthetic routes are within the scope of the disclosure. The material can be represented by $\text{Me}_a\text{Me}'_b\text{X}_c\text{F}$ and in the examples herein is embodied by a $\text{Cu}_3\text{Mo}_2\text{O}_9$ matrix. Other matrices and coatings are within the scope of this disclosure. For example, NiCuO_2 , Ni_2CuO_3 , and Cu_3TiO_4 .

The matrix and coating materials disclosed herein provide rechargeability to otherwise non-rechargeable metal fluoride matrix materials. Without being bound by a particular theory or mechanism of action, the rechargeability may be due to the electrochemical properties of the novel matrix, the coating of the metal fluoride to prevent copper dissolution, or a more intimate interface between the metal fluoride and the matrix material as a result of the heat treatment and reaction. Further, the novel matrix material may provide a kinetic barrier to the Cu dissolution reaction, or to similar dissolution reactions for other metal fluoride materials to the extent such dissolution reactions occur in the cycling of electrochemical cells.

In the case of oxide-based matrices (such matrices include those generated according to Formula II), intimate mixing of the metal fluoride and the metal complex (or other suitable precursor material) and moderate heat treatment can be used to generate rechargeable electrode materials. Other suitable precursors include materials that decompose to form metal oxides (and in particular, transition metal oxides) as opposed to using a metal oxide to directly react with the metal fluoride. Examples of such precursors include, but are not limited to, metal acetates, metal acetylacetonates, metal hydroxides, metal ethoxides, and other similar organo-metal complexes. In either event, the final rechargeable matrix material is not necessarily a pure oxide or a purely crystalline material. The reaction of Formula II predicts that there would not be a pure oxide or a purely crystalline material. In some instances, the metal oxide precursor or metal oxide material can form a coating, or at least a partial coating, on the metal fluoride active material. Without being bound by a particular theory or mechanism of action, the reaction of the metal oxide precursor or metal oxide material with the surface of the metal fluoride (and in particular copper fluoride) active material is important for generating a rechargeable electrode active material.

EXAMPLES

The following examples describe specific aspects of some embodiments of the invention to illustrate and provide a description for those of ordinary skill in the art. The examples should not be construed as limiting the invention, as the examples merely provide specific methodology useful in understanding and practicing some embodiments of the invention.

Example 1

Fabrication of Matrix and/or Coated Electrodes for Rechargeable Cells

Materials and Synthetic Methods.

All reactions were prepared in a high purity argon filled glove box (M-Braun, O_2 and humidity contents <0.1 ppm). Unless otherwise specified, materials were obtained from commercial sources (e.g., Sigma-Aldrich, Advanced Research Chemicals Inc., Alfa Aesar, Strem) without further purification.

Preparation of CuF_2 /Matrix.

Milling vessels were loaded with CuF_2 at from about 85 wt % to about 95 wt % and reactant (metal oxide or metal oxide precursor) at from about 5 wt % to about 15 wt %, and the vessels were sealed. The mixture was milled. After milling, samples were annealed at from about 200 degrees C. to about 575 degrees C. for 1 to 12 hours under flowing N_2 . Specific matrix reactants were processed as described below.

Preparation of $\text{CuF}_2/\text{Cu}_3\text{Mo}_2\text{O}_9$.

Milling vessels were loaded with CuF_2 (85 wt %) and MoO_3 (15 wt %), sealed, and then milled. After milling, samples were annealed at 450 degrees C. for 6 hours under flowing N_2 .

Preparation of CuF_2/NiO .

Milling vessels were loaded with CuF_2 (85 wt %) and NiO (15 wt %), sealed, and then milled. After milling, samples were annealed at 325 degrees C. for 6 hours under flowing N_2 .

Preparation of CuF_2 /Nickel(II) Acetylacetonate.

A fine dispersion of CuF_2 was prepared by milling in the presence of THF (40-120 mg CuF_2 /mL THF). The dispersed sample was then added to a solution of $\text{Ni}(\text{AcAc})_2$ in THF such that Nickel(II) acetylacetonate accounted for 15 wt % of the solids in the solution. The solution was then agitated by either shaking, sonication, or low energy milling for from about 1 to about 12 hours. The solution was then dried at room temperature under vacuum and the resulting solid was annealed at 450 degrees C. for 6 hours under dry air.

Electrode Formulation.

Cathodes were prepared using a formulation composition of 80:15:5 (active material:binder:conductive additive) according to the following formulation method: 133 mg PVDF (Sigma Aldrich) and about 44 mg Super P Li (Timcal) was dissolved in 10 mL NMP (Sigma Aldrich) overnight. 70 mg of coated composite powder was added to 1 mL of this solution and stirred overnight. Films were cast by dropping about 70 μL of slurry onto stainless steel current collectors and drying at 150 degrees C. for about 1 hour. Dried films were allowed to cool, and were then pressed at 1 ton/ cm^2 . Electrodes were further dried at 150 degrees C. under vacuum for 12 hours before being brought into a glove box for battery assembly.

Example 2

Electrochemical Characterization of Electrochemical Cells Containing Rechargeable Electrodes

All batteries were assembled in a high purity argon filled glove box (M-Braun, O_2 and humidity contents <0.1 ppm), unless otherwise specified. Cells were made using lithium as an anode, Celgard 2400 separator, and 90 μL of 1M LiPF_6 in 1:2 EC:EMC electrolyte. Electrodes and cells were electrochemically characterized at 30 degrees C. with a constant current C/50 charge and discharge rate between 4.0V and 2.0 V. A 3 hour constant voltage step was used at the end of each charge. In some instances, cathodes were lithiated pressing lithium foil to the electrode in the presence of electrolyte (1M LiPF_6 in 1:2 EC:EMC) for about 15 minutes. The electrode was then rinsed with EMC and built into cells as described above, except graphite was used as the anode rather than lithium.

FIG. 1 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the second cycle discharge capacity of three different cathode formulations containing a LiFePO_4 matrix is plotted as a function of LiFePO_4 content (labeled LFP) in the cathode in FIG. 1. The dotted line depicts the theoretical capacity of

LiFePO_4 . One cathode formulation is 100% LiFePO_4 . Another cathode formulation is a combination of CuF_2 and LiFePO_4 in which the content of LiFePO_4 was varied from 10% to 50% of the total weight of conductive material. The third cathode formulation is a combination of CuF_2 and the conventional conductive oxide MoO_3 and LiFePO_4 in which the content of LiFePO_4 was varied from 10% to 50% of the total weight of conductive material. As this is second cycle data, FIG. 1 demonstrates that all of the CuF_2 / LiFePO_4 matrices are rechargeable. In addition, the $(\text{CuF}_2/\text{MoO}_3)/\text{LiFePO}_4$ hybrid cathode containing 50% LiFePO_4 is also able to recharge. FIG. 1 further demonstrates a direct relationship between the capacity and the percent content of LiFePO_4 .

FIG. 2 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the voltage of a hybrid cathode is plotted against the capacity for the first and second cycles. The dashed line indicates the expected theoretical capacity from the LiFePO_4 content in cathode. The cathode formulation is the CuF_2 (70%)/ LiFePO_4 (30%) hybrid cathode from FIG. 1. During the first cycle, very little discharge capacity is observed, indicating that the LiFePO_4 material is not capable of accepting charge on this cycle. Without being bound to a particular theory or mechanism of action, the LiFePO_4 material may not accept charge as a result of defects introduced during milling. This data suggests that all of the capacity observed during the first and second cycles can be attributed solely to the CuF_2 .

FIG. 3 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the discharge capacity for cells with a range of LiFePO_4 content is plotted as a function of cycle for 10 cycles. The cathode formulation is CuF_2 with LiFePO_4 content ranging from 10% to 50% of the total weight of conductive material. FIG. 4 demonstrates that the hybrid cathode is able to consistently recharge across a number of cycles. Based on data from FIG. 2, it is expected that the discharge capacity is contributed solely by CuF_2 and not LiFePO_4 . This is a significant finding because CuF_2 has not been previously shown to have such significant reversible capacity. The combination of conductive matrix materials with CuF_2 renders the CuF_2 cathode material rechargeable.

FIG. 4 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the first and second cycle voltage traces for a cell containing a cathode formed from a metal fluoride and the new matrix material. In this case, the metal fluoride active material is CuF_2 and the matrix material is $\text{Cu}_3\text{Mo}_2\text{O}_9$. FIG. 4 demonstrates that the cell has about 140 mAh/g of reversible capacity. Previously known cathodes containing CuF_2 have not demonstrated such significant reversible capacity.

FIG. 5 illustrates the results of structural characterization of certain embodiments disclosed herein. Specifically, the powder X-ray diffraction pattern of the material forming the cathode tested in FIG. 4 is shown along with the powder X-ray diffraction patterns of CuF_2 and $\text{Cu}_3\text{Mo}_2\text{O}_9$. FIG. 5 demonstrates that the material contains phases rich in CuF_2 and phases rich in $\text{Cu}_3\text{Mo}_2\text{O}_9$. Thus, FIG. 5 demonstrates a new matrix material in combination with a metal fluoride active material. Further, grain size analysis of this powder X-ray diffraction data shows that the CuF_2 has a grain size greater than 130 nm. This is a significant finding since such comparatively large particles were thought to be too large to provide good electrochemical performance.

For many of the rechargeable matrices described herein (and in particular for matrices including Mo, Ni, or Ti), the reactions described herein yield a new matrix material at least at the surface of the particles of the metal fluoride active

material. The novel material present at least at the surface of the particles of the metal fluoride active material is believed to provided many of the benefits disclosed herein.

FIG. 6 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the second cycle discharge capacity of CuF_2 with various matrices and annealing temperatures. FIG. 6 shows many oxide matrices that provide recharge capability, demonstrated by capacities greater than 100 mAh/g.

Table 1 presents the results of further electrochemical characterization of certain embodiments disclosed herein. Table 1 shows that many metal oxide and metal oxide precursor starting materials can be used in the reactions described herein to yield rechargeable metal fluoride electrode materials. The materials in Table 1 include metal oxides, metal phosphates, metal fluorides, and precursors expected to decompose to oxides. In particular, nickel oxide showed excellent performance.

TABLE 1

Electrochemical Characterization of Various Precursor Materials as a Function of Anneal Temperature			
Matrix/Coating Precursor	Annealing Temp (C.)	Initial Capacity (0.02 C, Cy1, mAh/g)	Reversible Capacity (0.05 C, Cy2, mAh/g)
(NH ₄)H ₂ PO ₄	200	307	5
(NH ₄)H ₂ PO ₄	325	406	178
(NH ₄)H ₂ PO ₄	450	397	0
Al ₂ O ₃	200	281	70
Al ₂ O ₃	325	348	107
Al ₂ O ₃	400	203	78
AlF ₃	200	397	124
AlF ₃	325	384	125
AlF ₃	400	320	98
AlPO ₄	200	410	115
AlPO ₄	325	356	136
AlPO ₄	450	284	74
Bi ₂ O ₃	200	128	32
Bi ₂ O ₃	325	89	34
Bi ₂ O ₃	400	103	36
CaF ₂	200	301	86
CaF ₂	325	310	107
CaF ₂	400	282	125
CaO	200	1	1
CaO	325	138	27
CaO	400	84	29
Co ₃ (PO ₄) ₂	200	323	93
Co ₃ (PO ₄) ₂	325	373	161
Co ₃ (PO ₄) ₂	450	382	126
Co ₃ O ₄	200	167	112
Co ₃ O ₄	325	216	132
Co ₃ O ₄	450	329	151
Co ₃ O ₄	575	310	134
Cr ₂ O ₃	200	223	88
Cr ₂ O ₃	325	234	132
Cr ₂ O ₃	450	227	102
Cr ₂ O ₃	575	184	70
Fe Acetate	200	407	31
Fe Acetate	325	431	11
Fe Acetate	450	393	180
Fe ₂ O ₃	200	197	135
Fe ₂ O ₃	325	200	142
Fe ₂ O ₃	450	170	112
Fe ₂ O ₃	575	308	131
FeF ₂	200	427	202
FeF ₂	325	382	220
FeF ₂	400	370	155
FeF ₃	200	443	188
FeF ₃	325	406	218
FeF ₃	400	359	141
FePO ₄	200	252	76
FePO ₄	325	393	147
FePO ₄	450	429	197
In ₂ O ₃	200	250	64

TABLE 1-continued

Electrochemical Characterization of Various Precursor Materials as a Function of Anneal Temperature			
Matrix/Coating Precursor	Annealing Temp (C.)	Initial Capacity (0.02 C, Cy1, mAh/g)	Reversible Capacity (0.05 C, Cy2, mAh/g)
In ₂ O ₃	325	203	106
In ₂ O ₃	400	347	109
La ₂ O ₃	200	281	74
La ₂ O ₃	325	155	39
La ₂ O ₃	450	68	29
La ₂ O ₃	575	114	36
Li ₂ O	200	32	11
Li ₂ O	325	49	18
Li ₂ O	400	38	18
Li ₃ PO ₄	200	318	123
Li ₃ PO ₄	325	435	136
Li ₃ PO ₄	450	409	114
LiCoPO ₄	200	372	97
LiCoPO ₄	325	408	142
LiCoPO ₄	450	338	136
LiH ₂ PO ₄	200	300	111
LiH ₂ PO ₄	325	423	149
LiH ₂ PO ₄	450	387	107
LiMnPO ₄	200	351	77
LiMnPO ₄	325	368	102
LiMnPO ₄	450	397	178
LiNiPO ₄	200	402	116
LiNiPO ₄	325	396	191
LiNiPO ₄	450	405	176
MgF ₂	200	387	135
MgF ₂	325	378	147
MgF ₂	400	360	122
MgO	200	313	181
MgO	325	259	155
MgO	400	198	126
MnO	200	117	52
MnO	325	130	65
MnO	450	83	55
MnO	575	59	38
MnO ₂	200	120	76
MnO ₂	325	123	57
MnO ₂	450	242	150
MnO ₂	575	104	69
Mo Acetate	200	396	10
Mo Acetate	325	433	17
Mo Acetate	450	398	46
Na ₂ O	200	2	1
Na ₂ O	325	26	13
Na ₂ O	400	24	13
Ni	200	345	197
Ni	325	301	178
Ni	400	302	158
Ni	450	300	152
Ni acac	200	425	56
Ni acac	325	306	87
Ni Acac	400	247	30
Ni acac	450	362	172
Ni acetate	200	397	148
Ni acetate	325	376	46
Ni acetate	350	370	191
Ni acetate	400	383	180
Ni acetate	450	371	186
Ni acetate	500	373	171
Ni ₃ (PO ₄) ₂	200	410	124
Ni ₃ (PO ₄) ₂	325	430	52
Ni ₃ (PO ₄) ₂	450	126	44
Ni(C ₂ O ₂)	200	359	90
Ni(C ₂ O ₂)	325	395	195
Ni(C ₂ O ₂)	450	381	175
Ni(CP) ₂	200	304	27
Ni(CP) ₂	325	317	14
Ni(CP) ₂	450	258	148
Ni(OH) ₂	200	412	186
Ni(OH) ₂	325	362	196
Ni(OH) ₂	400	327	181
Ni(OH) ₂	450	300	169
NiBr ₂	200	125	0
NiBr ₂	325	225	78

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TABLE 1-continued

Electrochemical Characterization of Various Precursor Materials as a Function of Anneal Temperature			
Matrix/Coating Precursor	Annealing Temp (C.)	Initial Capacity (0.02 C, Cy1, mAh/g)	Reversible Capacity (0.05 C, Cy2, mAh/g)
NiBr2	400	244	113
NiCO ₃ *Ni(OH) ₂	200	380	17
NiCO ₃ *Ni(OH) ₂	325	359	215
NiCO ₃ *Ni(OH) ₂	450	317	184
NiF ₂	200	367	121
NiF ₂	325	395	207
NiF ₂	400	411	170
NiF ₂	450	396	177
NiO	125	257	131
NiO	200	403	222
NiO	225	384	212
NiO	250	385	221
NiO	275	370	229
NiO	300	335	175
NiO	325	402	252
NiO	350	365	209
NiO	375	260	123
NiO	400	371	200
NiO	425	361	186
NiO	450	386	183
NiO	500	308	150
NiO	575	319	112
None	200	181	30
None	325	394	216
None	450	247	61
Sb ₂ O ₃	200	111	34
Sb ₂ O ₃	325	147	37
Sb ₂ O ₃	400	223	104
Sc ₂ O ₃	200	359	159
Sc ₂ O ₃	325	293	159
Sc ₂ O ₃	400	84	33
Sc ₂ O ₃	450	150	68
Sc ₂ O ₃	575	55	17
ScF ₃	200	400	178
ScF ₃	325	387	174
ScF ₃	400	243	100
SiO ₂	200	1	1
SiO ₂	325	114	28
SiO ₂	400	230	92
SnO ₂	200	210	48
SnO ₂	325	182	68
SnO ₂	400	133	65
SrO	200	152	12
SrO	325	66	16
SrO	400	134	48
Ta ₂ O ₅	200	289	4
Ta ₂ O ₅	325	269	141
Ta ₂ O ₅	450	298	121
Ta ₂ O ₅	575	317	74
Ti(OEt) ₄	200	438	21
Ti(OEt) ₄	325	453	12
Ti(OEt) ₄	450	353	5
TiO ₂	225	322	150
TiO ₂	250	309	169
TiO ₂	275	262	162
TiO ₂	300	199	127
TiO ₂	325	322	173
TiO ₂	350	327	187
TiO ₂	375	120	77
TiO ₂	400	359	199
TiO ₂	425	345	194
TiO ₂	450	353	169
Y ₂ O ₃	200	353	130
Y ₂ O ₃	325	279	104
Y ₂ O ₃	450	83	37
Y ₂ O ₃	575	80	30
ZnF ₂	200	438	206
ZnF ₂	325	372	191
ZnF ₂	400	318	134
ZnO	200	210	95
ZnO	325	242	93
ZnO	400	194	44
ZnO	450	205	99

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TABLE 1-continued

Electrochemical Characterization of Various Precursor Materials as a Function of Anneal Temperature			
Matrix/Coating Precursor	Annealing Temp (C.)	Initial Capacity (0.02 C, Cy1, mAh/g)	Reversible Capacity (0.05 C, Cy2, mAh/g)
ZnO	575	151	71
ZrO ₂	200	302	122
ZrO ₂	325	288	129

FIG. 7 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, the second cycle discharge capacity for cells containing a cathode formed from a metal fluoride and the matrix material treated at different temperatures. In this case, the metal fluoride active material is CuF₂ and the matrix material is NiO. FIG. 7 shows a peak for cycle 2 capacity at about 325 degrees C. for NiO matrices, with nearly 250 mAh/g discharge capacity.

FIG. 8 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt % CuF₂ with 15 wt % of certain metal oxides (in this case NiO or TiO₂) at certain annealing temperatures. The mixtures were milled at high energy for about 20 hours. The anneal temperatures ranged from about 225 degrees C. to about 450 degrees C. and the anneal time was 6 hours. The 325 degree C. anneal temperature for the NiO starting material generated the best performance. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.02 C and over a voltage range of 2.0 V to 4.0 V.

FIG. 9 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt % CuF₂ with 15 wt % of certain metal oxides (in this case NiO or TiO₂) for certain annealing times. The mixtures were milled at high energy for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 1 hour, 6 hours, or 12 hours. The 6 hour anneal time yielded the best results for both the NiO and TiO₂ starting materials, and the NiO starting material generated better performance. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.02 C and over a voltage range of 2.0 V to 4.0 V.

FIG. 10 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, 90 wt %, or 95 wt % CuF₂ with 5 wt %, 10 wt %, 15 wt % of NiO. The mixtures were milled at high energy for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 6 hours. Using 10 wt % or 15 wt % of the NiO starting material generated better performance. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.02 C and over a voltage range of 2.0 V to 4.0 V.

FIG. 11 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO. The mixtures were milled at various energies comparable to milling on a Fritch Pulverizer.

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sette 7 Planetary Mill at 305, 445, 595, and 705 RPM for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 6 hours. Performance improves with increasing milling energy, suggesting that intimate physical interaction of the materials is required. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.05 C and over a voltage range of 2.0 V to 4.0 V.

FIG. 12 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO. The mixtures were milled for various times (3 hours, 20 hours, or 40 hours) at a high energy (comparable to 705 RPM on Fritch Pulverisette 7). The anneal temperature was 325 degrees C. and the anneal time was 6 hours. Performance does not improve after 20 hours of milling. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.05 C and over a voltage range of 2.0 V to 4.0 V.

FIG. 13 illustrates the results of electrochemical characterization of certain embodiments disclosed herein. Specifically, FIG. 13 shows the second cycle reversible capacity measured for various starting materials used to react with CuF₂. The starting materials include NiO, nickel(II) acetylacetonate, nickel acetate, nickel hydroxide, NiCO₃*Ni(OH)₂, Ni(C₂O₂)₂, Ni(CP)₂, and Ni. In some instances, the starting materials react to form a new phase. The materials react with the surface of the CuF₂ particles. Additionally, the anneal atmosphere was either N₂ or dry air. The precursor-type starting materials decompose to NiO (although this depends on the atmosphere for some precursors) at or below the annealing temperatures used for the reaction. The precursors that are soluble or have low boiling points can enable solution or vapor deposition processing methods. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.05 C and over a voltage range of 2.0 V to 4.0 V. Several materials show similar performance to the NiO baseline.

FIG. 14 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the second-cycle capacity retention and reversible capacity for cathode active materials formed from reacting CuF₂ with nickel(II) acetylacetonate using various processing conditions. In some cases, the CuF₂ was dispersed using methods described herein. The coatings were applied using mill coating techniques (that is, agitating the mixture in a milling apparatus) or by solution coating techniques (including solution coating driven by physisorption). All samples were annealed under dry air. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a rate of 0.05 C and over a voltage range of 2.0 V to 4.0 V. Testing demonstrates that solution coating methods can provide similar performance to the mill coating techniques.

FIG. 15 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the capacity as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO and for a control material. The NiO/CuF₂ mixture was milled at high energy for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 6 hours. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a cycle 1 rate of 0.02 C, a cycle 2 rate of 0.05 C, and a cycle 3 through cycle 25 rate of 0.5 C and over a voltage range of 2.0 V to 4.0 V. With the reacted NiO/CuF₂ as the active material, the cell cycles

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reversibly for extended cycling with capacity greater than 100 mAh/g for 25 cycles. Further, the reacted NiO/CuF₂ active material demonstrates retention of 80% of cycle 3 capacity as far out as cycle 15. The control material, which was prepared according to the process described in Badway, F. et al., *Chem. Mater.*, 2007, 19, 4129, does not demonstrate any rechargeable capacity. Thus, the material prepared according to embodiments described herein is significantly superior to known materials processed according to known methods.

FIG. 16 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, a galvanostatic intermittent titration technique (GITT) measurement for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO and for a control material. The NiO/CuF₂ mixture was milled at high energy for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 6 hours. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed over a voltage range of 2.0 V to 4.0 V at a rate of 0.1 C and with a 10 hour relaxation time. The GITT measurement relaxation points show low voltage hysteresis (about 100 mV), which indicate that the overpotential and/or underpotential are likely caused by kinetic and not thermodynamic limitations. This is consistent with other properties and characteristics observed for the reacted NiO/CuF₂ active material.

FIG. 17 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the capacity of full cells and half cells as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO. The NiO/CuF₂ mixture was milled at high energy for about 20 hours. The anneal temperature was 325 degrees C. and the anneal time was 6 hours. The label "Cu+2LiF" indicated that the NiO/CuF₂ electrode was lithiated by pressing Li foil to CuF₂ electrode in the presence of electrolyte as described above. The other half cell was lithiated electrochemically in the initial cycles. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed over a voltage range of 2.0 V to 4.0 V. Half cell performance is essentially identical between the two lithiation methods after cycle 2, while full cell shows additional irreversible capacity loss as compared to the half cells but similar capacity retention.

FIG. 18 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the voltage traces of the full cell and half cells prepared as described in relation to FIG. 17. The full cell has similar charge capacity to the half cells, but larger irreversible capacity loss and lower discharge voltage (which can indicate increased cell impedance). FIG. 18 demonstrates that the full cell has about 250 mAh/g of reversible capacity and about 500 mV hysteresis between charge and discharge plateau voltages.

FIG. 19 illustrates the results of electrochemical characterization of certain embodiments disclosed herein, specifically, the capacity retention of full cells and half cells as a function of cycle for cathode active materials formed from reacting 85 wt %, CuF₂ with 15 wt % of NiO. The results from a control material are also depicted. The full cell and half cells were prepared as described in relation to FIG. 17. The cells used a Li anode and an electrolyte containing 1M LiPF₆ in EC:EMC. The testing was performed at a cycle 1 rate of 0.1 C and over a voltage range of 2.0 V to 4.0 V. The capacity retention is essentially identical for the full and half cells of the NiO/CuF₂ active material. The control material shows essentially no rechargeable capacity.

While the invention has been described with reference to the specific embodiments thereof, it should be understood by

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those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention as defined by the appended claims. In addition, many modifications may be made to adapt a particular situation, material, composition of matter, method, or process to the objective, spirit and scope of the invention. All such modifications are intended to be within the scope of the claims appended hereto. In particular, while the methods disclosed herein have been described with reference to particular operations performed in a particular order, it will be understood that these operations may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the invention. Accordingly, unless specifically indicated herein, the order and grouping of the operations are not limitations of the invention.

The invention claimed is:

1. A composition comprising:

a particle comprising CuF_2 ; and

a surface coating on the particle, wherein the coating comprises a hybrid material formed by reacting via heat treatment the CuF_2 and a metal complex, the metal complex including Ni; and

wherein the hybrid material comprises Cu and Ni and wherein the composition has rechargeable capacity.

2. The composition of claim 1 wherein the reacting further comprises milling the metal fluoride material with the metal complex.

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3. The composition of claim 1 comprising a particle with a grain size greater than 100 nm.

4. The composition of claim 1 comprising a particle with a grain size greater than 130 nm.

5. The composition of claim 1 wherein the particle has a first phase and the coating has a second phase.

6. The composition of claim 5 wherein the first phase comprises CuF_2 .

7. The composition of claim 5 wherein the second phase comprises a material formed from the decomposition of the metal complex.

8. The composition of claim 1 wherein the metal complex comprises NiO.

9. The composition of claim 1 wherein the coating is covalently bonded to the particle.

10. The composition of claim 1 wherein the heat treatment is performed at a temperature less than 450 degrees C.

11. The composition of claim 1 wherein the heat treatment is performed at a temperature less than 325 degrees C.

12. A composition comprising:
a particle comprising CuF_2 ; and
a surface coating on the particle, wherein the coating comprises a material represented by a formula (1):



where $0 < a \leq 1$, $0 < b \leq 1$, $0 \leq c \leq 1$, and $0 \leq d \leq 1$:

wherein the composition has rechargeable capacity.

* * * * *